Measurement of Henry's Law Constant and Infinite Dilution Activity Coefficient of Isopropyl Mercaptan and Isobutyl Stripping Method

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Measurement of Henry's Law Constant and Infinite Dilution Activity Coefficient of Isopropyl Mercaptan and Isobutyl Mercaptan in Methyldiethanolamine (1) + Water (2) with w_1 = 0.25 and 0.50 at temperature of 298 to 348K using Inert Gas Stripping Method

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Abstract: In this study, the Henry's Law Constant and the activity coefficients in infinite dilution in a mass fraction of 25%, and 50% of methyldiethanolamine (MDEA) aqueous solution within the temperature range of 298-348 K at atmospheric pressure, were measured. An inert gas stripping method was used to perform all the measurements. The new values of Henry's Law Constant and the activity coefficients in infinite dilution correlation with solute molecular size were explained. The influence of the solvent is discussed taking into

consideration the heat of absorptions for different MDEA concentrations. Experimental results are compared to literature data wherever available.

***Keywords**:* solubility, limiting activity coefficient, heat of solution

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1. Introduction

Raw natural gas produced from gas fields always contains contaminants or other unacceptable substances including carbon dioxide, hydrogen sulfide, water, carbonyl sulfide, mercaptans (thiols), heavy hydrocarbons and mercury [1]. Removals of these contaminants are achieved through the acid gas treating/sweetening or gas purification process before it can be marketable. Currently, aqueous alkanolamine systems (amine systems) have been used extensively for the removal of acid gases from gas mixtures and it is considered as the most established technology [2-4]. The use of methyldiethanolamine (MDEA) for sour gas treatment is preferred due to its high equilibrium loading capacity and low heat of reaction with CO_2, hence lowering the energy requirement for regeneration [5-6].

Mercaptans are one of the contaminants found in sour gas which has to be removed in view of its toxicity which was reported to be similar to hydrogen sulfide [4]. In the context of growing concern on environmental issues, regulatory limits on gas emissions have been progressively reduced in line with the global trend towards more stringent specifications on gas impurities emissions from natural gas processing facilities. Huguet et al. [7] reported the specification of typical treated gas containing minor amounts of contaminants is as low as 2% CO_2, 2–4 ppm H_2S and 5–30 ppm total sulfur (mercaptans and COS). Furthermore, any mercaptans that are not absorbed from sour gas through the amine purification units complicate the process scheme for downstream liquid treatment units [8].

In response the trend, gas preconditioning upstream, or final step(s) for gas conditioning downstream of the gas-treating unit, are increasingly being considered as the better options to comply with the more stringent regulations [9]. Hence the study of solubility of sulfur components (in this study, mercaptans is considered) in amine systems will undoubtedly become increasingly important for the process designers and operators in order to conform to

the regulatory limits. According to Pellegrini, et al. [10], and Langè et al.[11], these restrictions have also led engineering companies to investigate the effects of these substances on the performances of amine systems.

Therefore it is crucial to understand the thermodynamic behaviour of mercaptans in amine solutions which will enable for selection to be made for the best solvent. This can be realized by considering the limiting activity coefficient (or Henry's law constant) and the activity coefficient at infinite dilution for mercaptans in amine solutions. These thermodynamic quantities served as important parameters for the design of separation process. Krummen et al [12] mentioned in his work that the separation of the final traces of components requires significant effort as the region within infinite dilution gives the least favourable values of the separation factor.

This work is the continuation of the previous works [13,14] in which we have determined the limiting activity coefficient of n-propylmercaptan, n-butyl mercaptan and dimethylsulfide in pure water and in 25 and 50 wt% concentration of methyldiethanolamine (MDEA) aqueous solution. The study focuses on the measurement of the Henry's law constant and the infinite dilution activity coefficient of isopropyl mercaptan and isobutyl mercaptan in a mass fraction of 25%, and 50% concentration in methyldiethanolamine (MDEA) aqueous solution within the temperature range of 298-348 K. The study of the mentioned systems will be able to evaluate the existence possibility of either physical or chemical absorption.

2. Experimental Section

2.1 Henry's Law Coefficient Measurements

For the determination of Henry's Law Constant and the Infinite Dilution Activity Coefficient, the experimental works were carried out in Mines ParisTech laboratory. The experiment employed the Gas Stripping method using a specially designed apparatus using

dilutor and saturator cell. This method is based on the evolution of vapor phase composition when the highly diluted solute of the liquid mixture in an equilibrium cell is stripped from the solution by a flow of inert gas (helium). The composition of the gas leaving the cell is periodically sampled and analyzed using gas chromatography. The peak area of the solute decreases exponentially with the volume of inert gas flowing out from the cell. Detailed descriptions of the principles and experimental apparatus have been discussed previously by Richon et al. [15, 16] and Krummen et al. [12]. Hence, only salient features will be highlighted in the paper.

2.2 Chemicals

For this study, the chemicals used are as presented in Table 1. No further purification of the chemicals were made. Ultra pure water was used which was purified and distilled through a Millipore (Direct Q5) osmosis membrane.

Table 1. Chemical sample

[INSERT TABLE 1 HERE]

Water and MDEA were degassed independently. Aqueous MDEA solutions of 25 wt% and 50 wt% were prepared under vacuum: respective masses of water and MDEA were determined by differential weighing to prepare a mass fraction (w) of 25 % and 50 % MDEA aqueous solution (mass fraction uncertainty lower than 0.001%).

2.3 Equipment

In this gas stripping method, two cells are immersed inside a liquid bath regulated to within 0.01 K. A platinum probe, in contact with the liquid phase of the “dilutor cell” connected to

an electronic display, is used for temperature readings. Temperature uncertainty of the probe was estimated; u(T) = 0.2 K. Analytical work was carried out using a gas chromatograph (PERICHROM model PR2100, France) equipped with a flame ionization detector (FID) connected to a data software system. The reference of the analytical column is: 15% APIEZON L, 80/100 Mesh (Silcosteel, length 1.2 m, diameter 2 mm) from RESTEK, France. Helium is used as the carrier gas in this experiment. The simplified flow diagram apparatus is as per shown in our previous paper [13].

In this experiment, a 40 cm^3 of pure solvent was introduced into the "saturator cell (S)" in upstream section, while about 25 cm^3 of the solute-solvent mixture was introduced into the "dilutor cell (D)"in the downstream section. A constant stripping gas "helium" flow adjusted to a given value by means of a mass flow regulator was bubbled through the stirred liquid phase and stripped the volatile solute into the vapor phase. The gas leaving the dilutor cell was periodically sampled and analyzed by gas chromatography using a rotating gas sampling valve [13].

Equilibrium must be reached between the gas leaving the cell and the liquid phase in the cell. This can be checked by verifying the measured activity coefficient value which does not depend on the eluting gas flow-rate. The peak area of solute decreased exponentially with time if the analysis is made within the linear range of the detector.

The Henry's Law coefficient, H_i (Pa), of solute *i* was calculated by means of equation 1 with assumption that the equilibrium has been reached between the gas leaving the cell and the liquid phase residing inside the cell. Equation 1 is obtained considering mass balance around the equilibrium cell concerning the solute.

$$H_i = -\frac{1}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right).\frac{RTN}{\frac{D}{1-\frac{P^{sat}_{solv}}{P}}+\frac{V_G}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right)} \quad (1)$$

where D is the carrier gas flow rate ($m^3 \cdot s^{-1}$); N is the total number of moles of solvent inside the dilutor cell; V_G (m^3) is the volume of the vapor phase inside the dilutor cell; S_i is the chromatograph solute i peak area; t (s) is the time; T (K) is the temperature inside the cell; P (101 300 Pa) is the pressure inside the cell (around 1 atm); P^{sat}_{solv} (Pa) is the saturation pressure of the solvent (see Appendix); and R ($J \cdot mol^{-1} \cdot K^{-1}$) is the ideal gas constant. Uncertainty concerning the Henry's law coefficient is estimated to be within 15 %. This estimation comes from propagation of errors on the uncertainty of the solute i peak area determination, the uncertainties on the flow, the uncertainties related to the temperature and pressure, number of moles of solvent and accuracy of the approach (mass balance and hypothesis, see Krummen et al. [11]) . It can be noticed that the expression given in the paper of Krummen et al. is wrong but only valid for measurement in non volatile solvent (Eq. 2).

$$H_i = -\frac{1}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right).\frac{RTN}{D\left(1+\frac{P^{sat}_{solv}}{P}\right)+\frac{V_G}{t}\ln\left(\frac{S_i}{(S_i)_{t=0}}\right)} \quad (2)$$

with $\frac{1}{1-\frac{P^{sat}_{solv}}{P}} \approx \left(1+\frac{P^{sat}_{solv}}{P}\right)$ for non volatile solvent (saturated pressure is very low, i.e. $\frac{P^{sat}_{solv}}{P} \ll 1$. The measurement for this work complied within very low saturated pressure condition where the range of $\frac{P^{sat}_{solv}}{P}$ for this work is within 0.03 -0.37).

This uncertainty is a consequence of the difficulty determining accurately the slope of the solute i peak area as a function of time [13]. The slope is determined by linear regression of area logarithms.

3. Experimental Results and Discussion.

3.1 Henry's Law Constant and Limiting Activity Coefficient in Infinite Dilution

Results tabulated in Tables 2 and 3 show the values of Henry's law constants for the isopropyl and isobutyl mercaptans in pure water and in aqueous solutions with MDEA concentration of

25% and 50% mass fraction of MDEA. In specific, Table 2 shows the data on isopropyl mercaptan whereas Table 3 on isobutyl mercaptan.

Figures 1 and 2 show the temperature dependence of the logarithm of the limiting activity coefficient as a function of inverse temperature for n-propyl mercaptan, isopropyl mercaptan n-butyl mercaptan and isobutyl mercaptan, in pure water and in aqueous solutions having similar concentrations as above i.e., mass fraction of 25% and 50% of MDEA. The limiting activity coefficient is calculated through equation 3. Details concerning the calculation of the saturation pressure are presented in the table shown in the Appendix.

$$\gamma_i^{\infty} = \frac{H_i^{P_{solv}^{sat}}}{P_i^{sat}} \quad (3)$$

Whilst Figures 5 and 6 show the temperature dependence of the logarithm of the Henry's law constants for isopropyl mercaptan and isobutyl mercaptan in pure water and in the same two MDEA aqueous solutions bearing the same concentrations.

The values of the Henry's law constants and limiting activity coefficient for n-propyl mercaptan and n-butyl mercaptan presented in these figures are taken from our previous work [13, 14].

Table 2. Temperature Dependence of Henry's Law Constant for in Isopropyl Mercaptan and n-propyl Mercaptan in Water and in (25 and 50) wt % MDEA aqueous Solutions:

u(T) =0.2K, u(H) = 15% of H (MPa)

[INSERT TABLE 2 HERE]

Table 3. Temperature Dependence of Henry's Law Constant for Isobutyl Mercaptan and n-butyl Mercaptan in Water and in (25 and 50) wt % MDEA aqueous Solutions :

u(T) =0.2K, u(H) = 15% of H (MPa)

[INSERT TABLE 3 HERE]

[INSERT FIGURE 1 HERE]

Figure 1. Logarithm of limiting activity coefficient of n-propyl mercaptan and isopropyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature (▲ water-iPM; × water-nPM;♦ 25 wt% MDEA-iPM; ■ 25 wt% MDEA-nPM ; ж 50 wt% MDEA-iPM; ● 50 wt% MDEA-nPM)

[INSERT FIGURE 2 HERE]

Figure 2. Logarithm of limiting activity coefficient of n-butyl mercaptan and isobutyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature. (▲ water-iBM; × water-nBM;♦ 25 wt% MDEA-iBM; ■ 25 wt% MDEA-nBM ; ж 50 wt% MDEA-iBM; ● 50 wt% MDEA-nBM)

The figures clearly showed that the values of the limiting activity coefficients for isopropyl and isobutyl mercaptans are smaller in MDEA aqueous solutions than in pure water. It can also be observed that the values of the limiting activity coefficient reduces with the increasing concentration of the aqueous amine solutions. The decreasing function of the amine concentration relation is true for all mercaptans considered in the study.

Bedell and Miller [17] carried out study on the mercaptans solubility in aqueous amine. The authors concluded that the solubility of mercaptans in amines can be treated as the sum of both a physical solubility and a chemical solubility. For isopropyl and isobutyl mercaptans, the absorption mechanisms observed involved physical and chemical. Due to the addition of MDEA to water, the alkalinity of the solution changes resulting in the increased of mercaptan solubility. It was also observed indirectly that the limiting activity coefficient increases with the solute molecular size (higher number of carbon atoms of mercaptans) at constant MDEA

concentration. The reason is due to the physical absorption being the predominant mechanism.

The comparison made on the values of the limiting activity coefficients for isobutyl mercaptan and n-butyl mercaptan showed that they were higher for the latter for both amine solutions i.e., concentration of 25 wt% and 50 wt%.

[INSERT FIGURE 5 HERE]

Figure 3. Logarithm of Henry's Law Constant of n-propyl mercaptan and isopropyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature.(▲ water-iPM; × water-nPM;♦ 25 wt% MDEA-iPM; ■ 25 wt% MDEA-nPM ; ж 50 wt% MDEA-iPM; ● 50 wt% MDEA-nPM)

[INSERT FIGURE 6 HERE]

Figure 4. Logarithm of Henry's Law Constant of n-butyl mercaptan and isobutyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature. (▲ water-iBM; × water-nBM;♦ 25 wt% MDEA-iBM; ■ 25 wt% MDEA-nBM ; ж 50 wt% MDEA-iBM; ● 50 wt% MDEA-nBM)

Figures 3 and 4 present the measured Henry's Law constant as a function of inverse temperature for n-propyl mercaptan, isopropyl mercaptan, n-butyl mercaptan and isobutyl mercaptan species in pure water and in 25 wt % and 50 wt % MDEA aqueous solution respectively. The values for n-propyl mercaptan and n-butyl mercaptan were taken from our previous work [13].

It was observed that the the Henry's Law constant for the various species of mercaptans exhibited lower values whilst in the MDEA solution compared to pure water. These effects

could be explained through the higher solubility of the mercaptans in the presence of alkanolamine in solutions as a result of higher affinity between the organic molecules namely the mercaptans and the alkanolamine, compared to water. The same deduction was made by Lange et. al [10] in their work on the influence of mercaptans impurities on thermodynamics of amine solutions. Bedell and Miller [17] mentioned in their work that in general the solubilities of higher mercaptans in pure water show a slight decrease in solubility as the mercaptan alkyl groups increase in size. Results obtained in this work are in fair agreement with their statement as higher mercaptans exhibited higher values of Henry's Law constant (as shown in Table 1 and 2). Higher Henry's Law constant values translate to lower solubilities of a gas in a solvent and vice versa.

Another important observation that could be made from Figure 3 is the higher Henry's Law constant exhibited by the isopropyl mercaptan compared to the n-propyl mercaptan which were consistent for both MDEA solutions i.e., 25 wt % and 50 wt % concentrations. The same observation was also made for the isobutyl and n-butyl mercaptans at 25 wt % and 50 wt % of amine concentration as shown in Figure 4. The Henry's Law constant for the former was also found to be higher. The significance of the result above is that the Henry's Law constant increases with the solute molecular size. Density of the two pairs showed that the n-propyl and the n-butyl display higher values compared to the iso-propyl and iso-buytl mercaptan as shown in Table 4. The higher density of n-butyl and n-propyl mercaptan species tend to have more compact molecular arrangement hence leading to smaller molecular size could fit more easily in the solvent cavity. These findings agree with the works by Tsonopoulos [18].

Table 4. Density of Isopropyl Mercaptan, n-propyl Mercaptan, Isobutyl Mercaptan and n-butyl Mercaptan at atm, 25^{o}C [19]

[INSERT TABLE 4 HERE]

The argument could also be further supported through the determination of the Hildebrand solubility parameter of the mercaptan species involved in the study as shown in Table 5. Theoretically, the solubility parameter is a numerical value that indicates the relative solvency behaviour of a specific solvent and it is derived from the square root of the cohesive energy density of the solvent [20]. Hildebrand solubility parameters obtained from literature [21] are calculated through equation 4.

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2} \quad (4)$$

where c is the cohesive energy density ; ΔH is heat of vaporization(kJ.mol^{-1}), V_m is molar volume of the mixture (m^3.mol^{-1}); T is the temperature (K) and R is the ideal gas constant (J.mol^{-1}.K^{-1}). By ranking solvents according to Hildebrand solubility parameter a solvent range is obtained, with solvents occupying positions in proximity to other solvents of comparable strength [19].

Table 5. Hildebrand Solubility parameter of Isopropyl Mercaptan, n-propyl Mercaptan, Isobutyl Mercaptan and n-butyl Mercaptan [21]

[INSERT TABLE 5 HERE]

Figures 5 shows the plotted values of the Henry's Law Constant and the limiting activity coefficient of the isobutyl mercaptan in water and in the various MDEA solution concentrations at different temperature (298-348 K). The figures are tendency curves that are useful for quick estimation of solubility and limiting activity coefficient value for the isobutyl mercaptan under different MDEA solution concentrations i.e., within the range of 0 - 15 mole

fraction (similarly to 0 - 50 wt %). Similar tendency curves can also be plotted for all the mercaptan species in this work.

[INSERT FIGURE 5 HERE]

Figure 5. Tendency curves of Henry's Law Constant Logarithm for isobutyl mercaptan in water and in various MDEA weight fractions at different temperature ♦ 298K ■ 323K ▲ 333K × 348K.

3.2 Heat of Solutions

To evaluate the effect of different concentration, the heat of solution is determined through equation 5. The equation is derived from the Gibbs-Helmholtz equation using excess thermodynamic properties.

$$\left(\frac{\partial\, lnH_i}{\partial {}^{1}/_{T}}\right)_{p} = \frac{\Delta H_i}{R} \qquad (5)$$

The heat of solution (ΔH_i(J.mol^{-1})) is also considered to be the partial molar excess enthalpy of component *i* in the solution. By assuming that the heat of solution is a constant and by integrating equation 6, it can be shown that limiting activity coefficient can be expressed as a function of 1/T.

$$lnH_i = A + \frac{B}{T} \qquad (6)$$

Which resulted in $\Delta H_i = RB$. Table 6 reported the results of the heat of solutions at different MDEA solution concentrations for isopropyl and isobutyl mercaptans.

Table 6. Values of Heat of Solution for isobutyl and isopropyl mercaptan in Different MDEA Molar Concentrations

[INSERT TABLE 6 HERE]

[INSERT FIGURE 6 HERE]

Figure 6. n-propyl, iso-propyl, n-butyl and iso-butyl mercaptans heats of solution as a function of MDEA molar concentration.(× nPM; ■ iPM; ▲ nBM; ♦ iBM)

Figure 6 shows the heats of solution for, n-propyl, isopropyl, n-butyl and isobutyl mercaptans as a function of MDEA concentration in mole fraction. From Table 6 and Figure 6, it can be observed that the heat of solution for n-compounds are higher than the iso-compounds for both propyl and butyl mercaptans at all different concentrations of MDEA solutions.

Also, it is known that the heat of solution are contributed by three effects namely a positive heat of cavitation, a negative heat of hydrophobic interactions, and the heat of reaction (here between acids R-SH and base (amines or water)) [16]. When MDEA is added in the aqueous solution, it is probable that the contribution of chemical reactions are increased as there is a change in the value of heat of solution. Another way to explain: the heat of solution is the sum of the contribution of breaking solute solute and solvent solvent interactions and creation of solvent solute interaction. Acid base reactions are also exothermic. The two first are endothermic and the last one is exothermic. According to Table 6 the final results show that more energy is releasing during the solvation probably due to acid base reaction.

Moreover, in pure water, the difference in the heat of solution is due to the size effect (physical solubility) causing the partial molar excess enthalpy to be slightly higher for the iso-compound. In addition, with higher value of Henry's Law Constant shown by isobutyl and isopropyl mercaptan, indicates that the solute are less soluble in the alkanolamine solution thus less energy required to remove the solute from the solution. It is also observed that heat

of solution for isopropyl and isobutyl mercaptans have the same order of magnitude and the same shape.

As for the both iso and n-propyl and butyl mercaptan, the n-butyl and isobutyl mercaptan shows a higher heat of solution values due to the presence of an additional alkyl group compared to the n-propyl and isopropyl mercaptan.

4. Conclusion

The new values for Henry's Law constants and the infinite dilution activity coefficients of n-propyl mercaptan, isopropyl mercaptan n-butyl mercaptan, isobutyl mercaptan in 25 wt % and 50 wt % MDEA aqueous solution at T = (298 to 348 K) have been obtained through gas stripping measurements. Based on general observation, it can be concluded that that the limiting activity coefficient and Henry's Law constant is an increasing function of the solute molecular size value. The observation can be supported through the determination of Hildebrand solubility parameter for the components and solvent involved. The experimental technique has provided information about heats of solution of MDEA aqueous solution.

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Appendix

Correlation used to calculate vapor pressure is

$$P^{sat} = e^{\left(A+\frac{B}{T}+C\ln(T)+D\cdot T^{E}\right)}$$

with the following parameters (Table 7) ;

Concerning the solvent, the expression is

$$P^{sat}_{solv} = x_{water}P^{sat}_{water} + x_{MDEA}P^{sat}_{MDEA}$$

Table 7: Vapor pressure correlation parameters.

[INSERT TABLE 7 HERE]

These parameters (for the mercaptans) were obtained after adjustment on literature data (from ThermoDataEngine version 3.0 from NIST) by minimising the objective function,

$$F = \sum\left(P_{\exp} - P_{cal}\right)^2$$

The AAD (average absolute deviations) are presented in the following Table 8:

Table 8: Average absolute deviations (AAD) values .

[INSERT TABLE 8 HERE]

References

[1] Ryzhikov A., Hulea V., Tichit D., Leroi C., Anglerot D., Coq B., Trens P., Applied Catalysis A: General 397 (2011) 218–224

[2] Deshmukh, R.D. and Mather A.E., Chem. Eng. Sci. 36 (1981) 355–362.

[3] Kumar S., Cho J. H, Il Moon., Int. Journal of Greenhouse Gas Control 20 (2014) 87–116

[4] Abass A. Olajire, Energy 35 (6) (2010), 2610–2628

[5] Paul, S.; Mandal, B. J. Chem. Eng. Data 51, (2006) 1808–1810

[6] Ayyaz M, Mohamed I. l , Thanabalan M., Amir S. J. Chem. Eng. Data 54 (2009) 2317–2321

[7] Huguet E., Coq B., Durand R., Leroi C., Cadours R., Hulea V., Applied Catalysis B: Environmental 134– 135 (2013) 344– 348

[8] Awan A. J, Kontogeorgis G. M., Tsivintzelis I., Coquelet C., Ind. Eng. Chem. Res. 52 (2013) 14698−14705

[9] Awan A. J, Tsivintzelis I, Valtz A., Coquelet C., Kontogeorgis G. M., Ind. Eng. Chem. Res 51 (2012) 11561−11564

[10] Pellegrini, L.A., Langè S., Moioli, S.,Picutti, B., Vergani, P., Industrial and Engineering Chemistry Research 52 (2013) 2018-2024.

[11] Langè S., Pellegrini, L.A., Moioli, S., Picutti, B., Vergani, P., Industrial and Engineering Chemistry Research (2013), 52 (5), 2025–2031

[12] Krummen, M.; Gruber, D.; Gmehling, J. Ind. Eng. Chem. Res. 39 (2000) 2114-2123

[13] Coquelet C., D. Richon., J. Chem. Data 50 (2005) 2053-2057

[14] Coquelet C., S.Laurens, D. Richon., J. Chem. Data 53 (2008) 2540-2543

[15] Richon, D.; Antoine, P.; Renon, H. Ind. Eng. Chem. Process Des. Dev. 19 (1980) 144-147

[16] Richon, D.; Renon, H. J. Chem. Data. 25 (1980) 59-60

[17] Bedell S A., Miller M., Ind. Eng. Chem. Res. 46 (2007) 3729-3733

[18] Tsonopoulos C., Fluid Phase Equilibria 186 (2001) 185–206

[19] Stephenson, Richard M.; Malanowski, Stanislaw**,** Handbook of the Thermodynamics of Organic Compounds (1987)

[20] Burke, J. AIC Book Paper Group Annual 1984, 3, 13-58

[21] Daubert, T. E., Danner, R. P., Sibul, H. M., & Stebbins, C. C. DIPPR Data compilation of pure compound properties. DIPPR, AIChE, New York (1993).

Table 1. Chemical sample

Chemical Name	Cas No.	Mass Fraction Purity	Supplier
Isopropyl Mercaptan	75-33-2	>0.99	Aldrich
Isobutyl Mercaptan	513-44-0	>0.99	Aldrich
Methyl Diethanolamine	105-59-9	99 + GC%	Aldrich

Table 2. Temperature Dependence of Henry's Law Constant for in Isopropyl Mercaptan and n-propyl Mercaptan in Water and in (25 and 50) wt % MDEA Aqueous Solutions

T/K	H/MPa	u(H)/MPa	γ∞	T/K	H/MPa	γ∞
Isopropyl Mercaptan				**n-propyl Mercaptan**		
Water						
298.5	35	5.3	916	293.1	24	1455
308.3	54	8.1	1005	303.1	47	1844
318.3	76	11.4	999	333.1	94	1191
323.3	88	13.2	988			
333.3	103	15.5	840			
348.2	143	21.5	730			
Aqueous MDEA solution						
25 wt%				**25 wt%[a]**		
298.5	8.6	1.3	227	298.1	4.3	209
308.3	13	2.0	244	303.1	5.4	211
318.4	17	2.6	229	313.1	6.9	181
323.4	20	3.0	225	323.1	10	187
333.5	28	4.2	222	333.1	15	189
348.2	43	6.5	220	343.1	17	157
50 wt%				**50 wt%[b]**		
298.6	3.6	0.5	94	293.1	3.1	188
308.2	5.3	0.8	98	298.0	3.9	190
318.3	8.3	1.2	109	303.1	4.3	168
323.6	9.1	1.4	101	312.9	4.9	129
333.5	11	1.7	91	323.1	5.6	101
348.0	17	2.6	85	333.1	9	105
				343.1	10	93

u(T) = 0.2K, u(H) = 15% of H (MPa)

[a]*Results from Coquelet et al. [13]*

[b]*Results from Coquelet and Richon[14]*

Table 3. Temperature Dependence of Henry's Law Constant for Isobutyl Mercaptan and n-butyl Mercaptan in Water and in (25 and 50) wt % MDEA Aqueous Solutions

T/K	H/MPa	u(H)/MPa	γ∞	T/K	H/MPa	γ∞
	Isobutyl Mercaptan			**n-butyl Mercaptan[a]**		
			Water			
298.3	54	8.1	5803	292.8	29	6223
308.3	80	12	5462	312.8	70	5717
323..4	138	20.7	5046	332.8	125	4504
333.2	204	30.6	5145			
348.1	310	46.5	4674			
			Aqueous MDEA solution			
		25 wt%			**25 wt%[a]**	
294.0	5.5	0.8	669	293.1	3.4	708
298.5	7.0	1.1	665	303.1	4.9	622
303.5	7.9	1.2	599	313.1	7.8	623
313.4	12	1.8	610	318.1	10	644
318.4	16	2.4	635			
323.5	20	3.0	647			
333.4	28	4.2	633			
348.1	42	6.3	638			
		50 wt%			**50 wt%[b]**	
298.6	2.9	0.4	272	292.8	1.8	383
308.4	4.2	0.6	255	302.6	3.2	411
318.5	7.1	1.1	282	312.7	3.1	253
323.2	7.7	1.2	252	322.9	4.7	246
333.4	11	1.7	238	332.4	7.2	262
348.3	16	2.4	208	342.8	9.3	241

u(T) = 0.2K, u(H) = 15% of H (MPa)

[a]*Results from Coquelet et al. [13]*

[b]*Results from Coquelet and Richon[14]*

Table 4. Density of Isopropyl Mercaptan, n-propyl Mercaptan, Isobutyl Mercaptan and n-butyl Mercaptan at atm, 25^{o}C [19]

Component	Density / g.cm^{-3})
n-propyl Mercaptan (nPM)	0.841
isopropyl Mercaptan (iPM)	0.820
n-butyl Mercaptan (nBM)	0.842
isobutyl Mercaptan (iBM)	0.831

Table 5. Hildebrand Solubility parameter of Isopropyl Mercaptan, n-propyl Mercaptan, Isobutyl Mercaptan and n-butyl Mercaptan [21]

Component	Hildebrand Parameter δ /cal$^{1/2}$.cm$^{-3/2}$
n-propyl Mercaptan (nPM)	8.81
isopropyl Mercaptan (iPM)	8.30
n-butyl Mercaptan (nBM)	8.70
isobutyl Mercaptan (iBM)	8.43
Water	22.9
MDEA	13.8
Aqueous MDEA (25 wt%)	22.5
Aqueous MDEA (50 wt%)	21.7

Table 6. Values of Heat of absorption for isobutyl and isopropyl mercaptan in Different MDEA Molar Concentrations

Aqueous MDEA solution /wt %	Heat of solution /kJ.mol^{-1}			
	iBM	nBM[a]	iPM	nPM[a]
0	-30.6	-29.7	-26.2	-26.0
25	-32.8	-33.5	-27.6	-26.9
50	-30.2	-26.3	-24.7	-18.4

[a]Results from Coquelet and Richon[14].

Table 7: Vapor pressure correlation parameters.

Parameter	nBM*	iBM*	nPM*	iPM*	Water**	MDEA**
A	64.649	61.213	61.813	74.676	73.649	253.07
B	-6262	-5909	-5623	-5272	-7258.2	-18378
C	-6.1280	-5.6431	-5,7934	-8.1974	-7.3037	-33.972
D	6.84×10^{-18}	1.48×10^{-17}	6.51×10^{-18}	3.42×10^{-16}	4.17×10^{-6}	2.33×10^{-5}
E	6	2	6	6	2	2

* Temperature ranges for vapor pressure data underlying the correlation T(K) for mercaptan species ;
nBM: 323.1-408.8 , iBM: 310.5-394.6 , nPM; 284.6-383.2, iPM; 283.8 -358.9
** From Daubert et al. [21]

Table 8: Average absolute deviations (AAD) values

	nBM	**iBM**	**nPM**	**iPM**
AAD /%	2	1	3	6

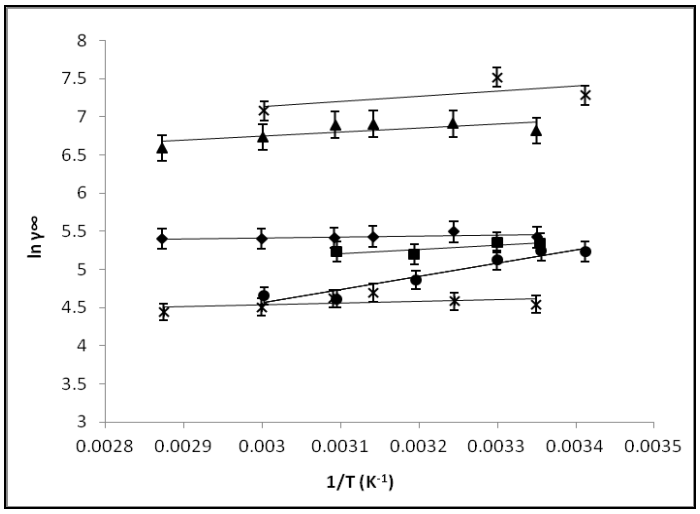

Figure 1. Logarithm of limiting activity coefficient of n-propyl mercaptan and isopropyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature (▲ water-iPM; × water-nPM;♦ 25 wt% MDEA-iPM; ■ 25 wt% MDEA-nPM ; ж 50 wt% MDEA-iPM; ● 50 wt% MDEA-nPM)

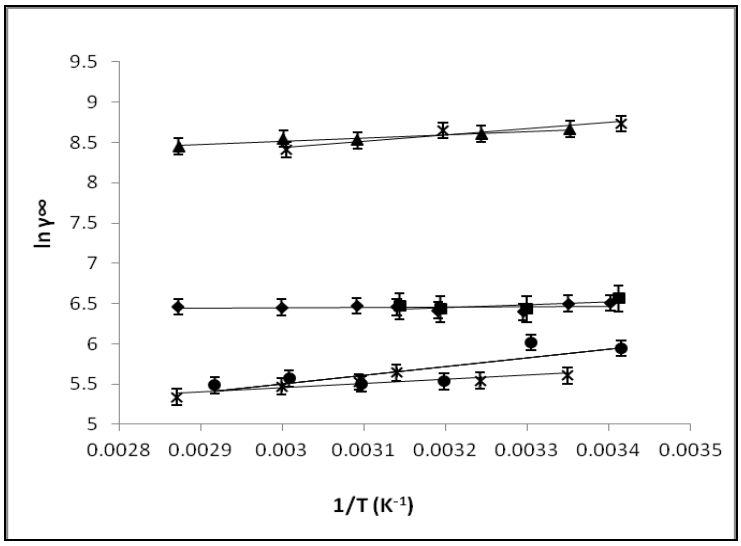

Figure 2. Logarithm of limiting activity coefficient of n-butyl mercaptan and isobutyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature. (▲ water-iBM; × water-nBM;♦ 25 wt% MDEA-iBM; ■ 25 wt% MDEA-nBM ; ж 50 wt% MDEA-iBM; ● 50 wt% MDEA-nBM)

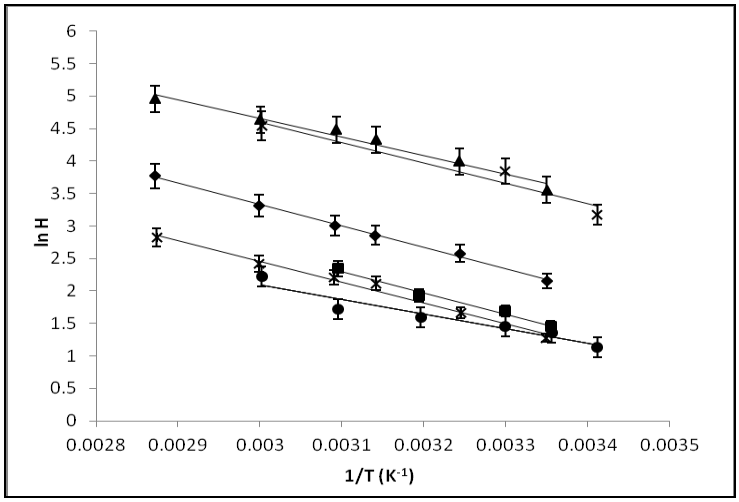

Figure 3. Logarithm of Henry's Law Constant of n-propyl mercaptan and isopropyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature.(▲ water-iPM; × water-nPM;♦ 25 wt% MDEA-iPM; ■ 25 wt% MDEA-nPM ; ж 50 wt% MDEA-iPM; ● 50 wt% MDEA-nPM)

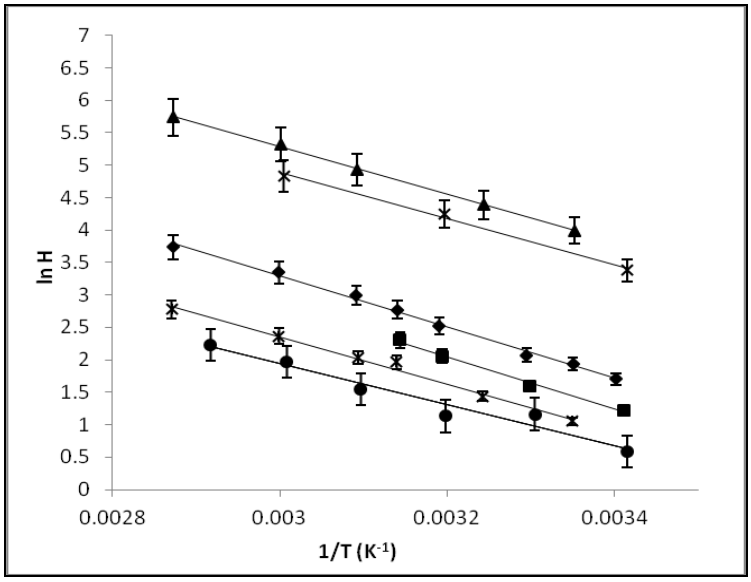

Figure 4. Logarithm of Henry's Law Constant of n-butyl mercaptan and isobutyl mercaptan in water and in various MDEA weight fractions of 25 %; and 50 % as a function of inverse temperature. (▲ water-iBM; × water-nBM;♦ 25 wt% MDEA-iBM; ■ 25 wt% MDEA-nBM; ж 50 wt% MDEA-iBM; ● 50 wt% MDEA-nBM)

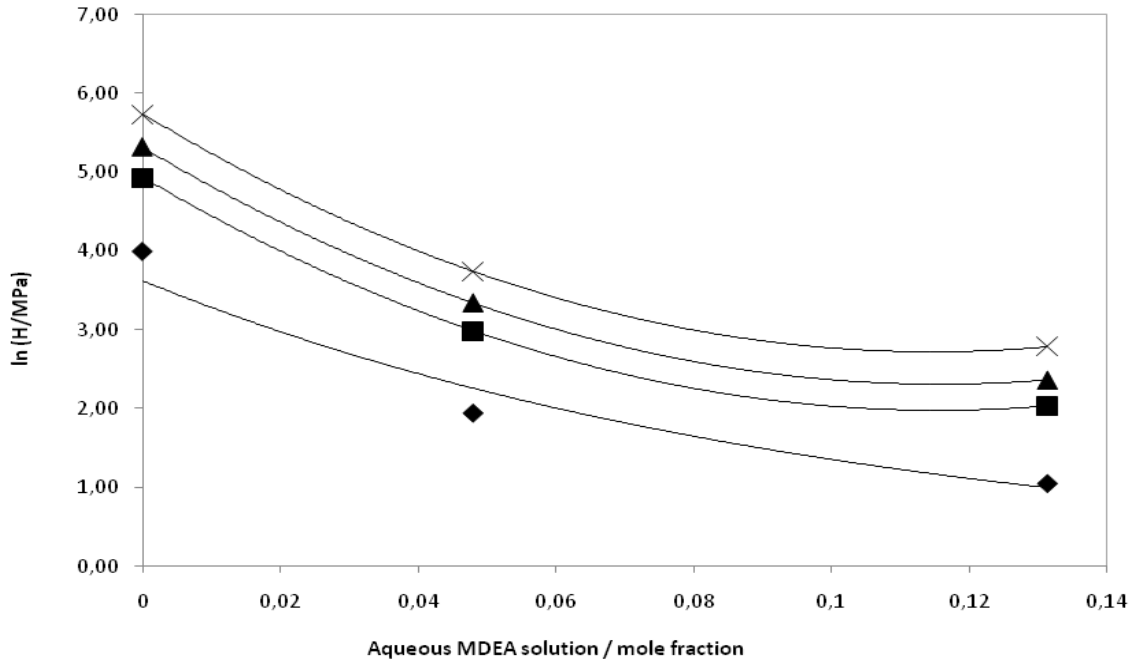

Figure 5. Tendency curves of Henry's Law Constant Logarithm for isobutyl mercaptan in water and in various MDEA mole fractions at different temperature ♦ 298K ■ 323K ▲ 333K × 348K**.**

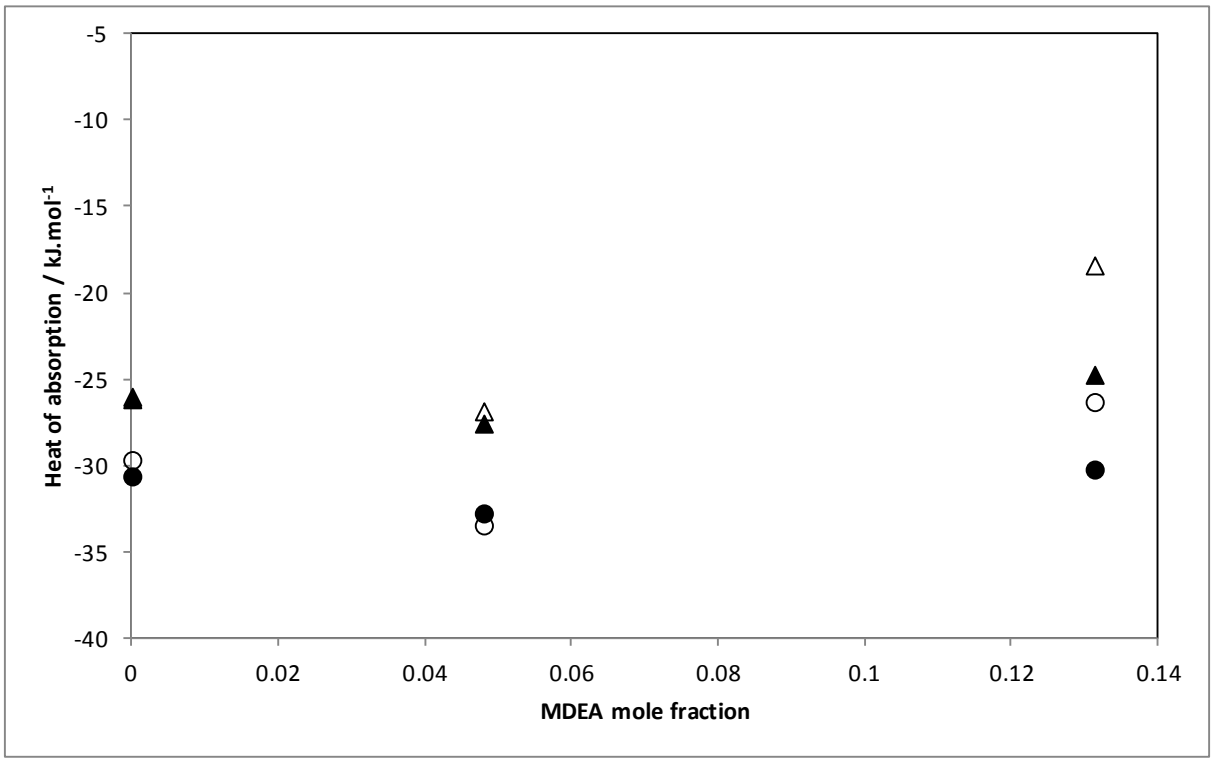

Figure 6. n-propyl, iso-propyl, n-butyl and iso-butyl mercaptans heats of solution as a function of MDEA molar concentration.(Δ nPM; ▲ iPM; ○ nBM; ● iBM)